(51) International Patent Classification ^{4} : C04B 41/87, 35/10	A1	(11) International Publication Number: WO 88/ 02742
		(43) International Publication Date: 21 April 1988 (21.04.88)

(72) Inventors: MARTIN, Corrie, B. ; 321 N.E. 59th Street, Seattle, WA 98105 (US). AKSAY, Ilhan, A. ; 3729 N.E. 194th Street, Seattle, WA 98155 (US).

(54) Title: METHOD FOR PRODUCING A SURFACE-TOUGHENED CERAMIC COMPOSITE

(57) Abstract

A novel method for producing surface-toughened ceramics by infiltration, using a sol or solution of a polymorphic ceramic material such as zirconium oxide. Porous ceramic compacts are infiltrated with the sol or solution by introducing the sol or solution into the compact under vacuum or by using pore pressure. Properties of the infiltrated ceramics may be optimized by varying parameters, including pore size distribution and volume of porosity of the porous compact, the viscosity of the ceramic sol or solution used for infiltration, and the number of infiltration cycles. The ceramic composites which are produced contain zirconium oxide retained in metastable phase near the surface of the composite, and exhibit high strength.

METHOD FOR PRODUCING A SURFACE-
TOUGHENED CERAMIC COMPOSITE

Field of the Invention

This invention relates to surface toughened ceramics, particularly
to zirconia infiltrated alumina composites exhibiting high strength, and to a
method for preparing such composites.

Background of the Invention

For many applications, it is desirable to improve the strength and
toughness of a ceramic to improve characteristics such as resistance to
temperature change, for example, where the ceramic is used in machine parts.
Surface toughening is one mechanism which has been developed, using the
material zirconium oxide (ZrO_2) (hereafter referred to as "zirconia") in a
ceramic matrix such as aluminum oxide (Al_2O_3) (hereafter referred to as
"alumina"). Garvie et al., Nature, 158 (12), p.703-704 (1975). Zirconia is a
polymorphic ceramic material existing in tetragonal, monoclinic and cubic
crystal form. The tetragonal structure of zirconia prevails at higher tempera-
tures. As the zirconia particles cool after fabrication, polymorphic phase
transformation occurs, resulting in predominance of the monoclinic crystal
structure, with a concomitant increase in volume. For pure zirconia, the
transformation occurs at about 1200°C and ends at about 600°C. Lange, J.
Material Science, 17, p.225-254 (1982), incorporated by reference herein.

Recently, work has been done using metastable grains of tetragonal
zirconia held within a surrounding matrix of varying ceramic composition by
mixing zirconia and alumina powders together. The grains of zirconia are in the
tetragonal rather than monoclinic phase, even though the temperature is below
the unconstrained equilibrium transformation temperature range at which
zirconia exists in monoclinic form. The metastable condition is obtained by
surrounding fine grains of zirconia as inclusions in a constraining matrix such as
alumina. The matrix constrains the grains of zirconia, preventing the volume
changes associated with the transformation to the monoclinic form. The

presence of tetragonal grains or inclusions of zirconia in a ceramic increases the fracture toughness of the material by decreasing propagation of cracks as it increases the energy required for the crack to propagate. Thus, if a crack commences in the ceramic composite, metastable grains of tetragonal zirconia

5   adjacent to the crack transform to the stable monoclinic structure. The stress induced transformation increases the ceramic's fracture toughness.

Lange derived a phase field diagram illustrating the resultant mechanisms of the polymorphic phase transformation of zirconia in an alumina matrix based on zirconia inclusion size and the chemical energy of the system.

10   Lange, supra, p.233. This diagram demonstrates the importance of small inclusions with a narrow distribution of sizes of zirconia particles with respect to the fraction of zirconia retained in the tetragonal state. For example, there is a metastable particle size where transformation will not occur, even at low temperature. Obtaining such a narrow distribution requires increased processing

15   efforts, increased amounts of raw materials, and additional manufacturing time. Thus, the codispersion techniques previously used require submicron size zirconia particles to maintain the tetragonal form of zirconia in the finished composite.

Table I provides the critical transformation size of zirconia particles in an alumina matrix with respect to the volume percent (v/o) of

20   zirconia, as well as an accepted, unconstrained (for particles not held in a matrix) critical particle size. Garvie et al., Nature, 258, p. 703-704 (1975); Lange, J. Materials Sci., 17, p. 225-234 (1982). Therefore, in order to maintain a sufficient percentage of zirconia in the metastable tetragonal structure in the finished ceramic body, it is preferred that the zirconia grains are relatively

25   small in size (i.e., in the submicron range).

TABLE I
Critical Inclusion of Grain Size

v/o ZrO$_2$	Size (μ)
100	0.03 D$_{uc}$
5	2.3
10	1.35
15	0.85
20	0.74

where v/o = volume percent zirconia within an alumina matrix;

μ_c = size of constrained zirconia particles taken from Lange, supra; and,

D_{uc} = an accepted unconstrained critical particle size taken from Garvie, supra.

As can be seen from Table I the amount of metastable tetragonal zirconia that can be retained in the matrix decreases as the volume percent of zirconia in the ceramic composite increases. Thus, restrictions on grain size and volume percent of zirconia have reduced the practicality and toughness of prior alumina/zirconia ceramic composites. In an attempt to overcome these difficulties, Lange, U.S. Patent No. 4,316,964, utilized zirconia, stabilized by a rare earth oxide dissolved in the zirconia, to maintain some of the zirconia in the tetragonal structure. The rare earth oxide increases the critical transformation size (the size of zirconia particles above which transformation will occur). The balance of the ceramic composite was alumina. Using this method, composites were obtained with higher strength than that of previous composites; however, as mentioned above, this method requires the use of additional materials, such as the rare earth oxides, and additional time to carry out the procedure. In addition, the use of a stabilizing agent can decrease the chemical free energy change to the point where tetragonal particles will not transform under any conditions which, in turn, prevents the desired toughening.

Typically, the results of previous methods used to fabricate ceramic composites of alumina-zirconia composites, such as codispersion and mixed sol processes, have been homogenous composites, with zirconia distributed throughout the ceramic body. Since critical stresses are usually achieved at the outside tensile face of the body, however, it is not necessary to provide a toughening mechanism (i.e., metastable zirconia) throughout the entire body. Therefore, if a homogenous composite layer containing zirconia, for example, exists at this critical face only, leaving the internal core of the body as a single phase, the resulting composite may have a higher strength-to-weight ratio. This type of composite is seen in nature in the structure of bone, which has a dense surface layer with a porous lightweight core. Thus, composites toughened at the surface with material such as zirconia in metastable phase should result in a stronger and lighter ceramic.

Therefore, more efficient and economical methods which do not require additional raw materials or increased manufacturing time are needed to prepare toughened composite ceramics.

Summary of the Invention

Accordingly, the present invention provides a method for preparing surface-toughened composite ceramics by infiltrating porous ceramic compacts with a zirconia sol. Infiltrated compacts are heat treated and may be sintered to form a surface-toughened composite ceramic with high strength and lowered density. Infiltration is carried out in a vacuum or using a wicking process. The properties of the composite may be optimized by varying the porosity of the compact, the heat treatment and sintering temperatures, the viscosity of the zirconia sol, or the amount of zirconia infiltrated into the porous compact.

Brief Description of the Drawings

The present invention will be described in connection with the accompanying drawings in which:

FIGURE 1 is a SEM micrograph of zirconia particles in suspension;

FIGURE 2 is a graph illustrating percentage weight loss of heat-treated zirconia infiltrated ceramics;

FIGURE 3 gives the increase in volume percent of zirconia as a function of infiltration frequency;

FIGURE 4 illustrates the tetragonal fraction of zirconia as a function of the number of infiltrations over a given percent theoretical density range;

FIGURE 5 depicts densification as a function of the amount (number of cycles) of zirconia introduced by infiltration during sintering;

FIGURE 6 shows isothermal sintering effects on the fraction of zirconia retained in the tetragonal phase;

FIGURE 7 is a graph showing relative quantities of zirconia as a function of depth within the composite obtained from EDAX readings on sample cross sections; and,

FIGURES 8a-e are SEM micrographs showing the grain size distribution in a sample composite.

Detailed Description of the Invention

To carry out the process of the present invention, a porous ceramic compact is formed from a suitable ceramic precursor material such as alumina. This porous compact is then infiltrated with a sol of a polymorphic ceramic material, such as zirconia, that toughens the resulting structure. The invention is set forth in greater detail in the description and the examples which follow.

The infiltrated ceramic composites of the present invention preferably consist essentially of from approximately 1 to 15 volume percent (based on the total volume of the ceramic) of a polymorphic ceramic material

such as zirconia, the balance being a ceramic matrix of a ceramic material such as alumina. The infiltrated zirconia is preferably present in from 100 down to 10 percent substantially tetragonal phase. The infiltration of zirconia into the surface contributes to the toughness and high strength of the ceramic composites produced. The properties of the final composite are a function of the amount of zirconia infiltrated into the surface and the fraction of zirconia retained in metastable tetragonal phase. In turn, the amount of zirconia infiltrated into the ceramic, and the amount retained in tetragonal phase, may be optimized by repeating infiltration and by controlling other parameters such as viscosity of the zirconia sol, porosity and pore size distribution of the compacts infiltrated with zirconia, and by varying the temperature and duration of heat treatment and sintering of the infiltrated compacts.

Preparation of a Porous Ceramic Compact for Infiltration

Conventional procedures are used to prepare a porous ceramic compact. For example, the porous compact may be prepared from a colloidal suspension of a suitable, cold pressed ceramic material, or may be made by hot pressing techniques. Porous ceramic compacts of different porosities and pore size distributions may also be obtained from commercial sources. Suitable ceramic materials for preparing the porous compact include alpha alumina, beta alumina, and material designated as "active refractories" in U.S. Patent No. 4,415,673, by Feagin, the disclosure of which is incorporated by reference herein, or any other suitable ceramic material. The suspension may be sterically or electrostatically stabilized to prevent flocculation, for example, by using anionic ceramic surfactants such as Darvan C and citric acid.

In a preferred technique, a colloidal suspension of alpha alumina is consolidated to form a "green" compact by removing liquid from the suspension by conventional slip casting, using a plaster of paris filter, to form the desired shape. After consolidation, the samples are dried and may be partially sintered at a high temperature to form a porous compact. Alternatively, unsintered porous compacts may be used after filtration and drying for infiltration. Variations in porosity may be accomplished by altering temperature, time and particle size distribution. For example, partially sintering the green compacts at several different temperatures has been shown to produce a range of pore sizes for compacts formed from alpha alumina powders with bimodal particle size distributions. Han (Sintering of Bimodal Compacts, Thesis submitted for Master's Degree, University of California, Los Angeles, CA, (1985)). The porous compact may be shaped using conventional techniques for further processing, as described below.

Infiltration

Preferably, infiltration is accomplished using a sol of polymorphic ceramic material such as stabilized or unstabilized zirconia. A sol, as used herein, designates a suspension containing fine (submicron) particles. Sols of polymorphic ceramic material, such as zirconia, may be prepared by making a 5-20 weight percent zirconia suspension of various viscosities. In the present invention, sols containing 15 to 20 weight percent zirconia in viscosity ranges of 5 centipoise to 100 centipoise, and with zirconia particle sizes ranging from 10 Å to 100 Å, are preferred. The sols may be stabilized to retain larger particles of zirconia in tetragonal phase, e.g., by adding rare earth oxides such as ytria or halfnia, or may be unstabilized. Infiltration may also be accomplished using a solution in place of a sol. A solution consists of a dispersion of molecular units of a substance, for example, a zirconium salt. Alternatively, a polymeric solution of a ceramic precursor, for example, a partially hydrolyzed solution of zirconium alkoxide, or a polymer containing zirconium such as a zirconium oxy-alkoxy polymer, may be used for infiltration.

The porous ceramic compacts prepared as above, partially sintered or unsintered, are infiltrated by the sols or solutions of zirconia. In a preferred embodiment, the porous ceramic compact selected for infiltration is placed in a vacuum and maintained prior to infiltration for a suitable amount of time to ensure evacuation of pores. It is preferable to introduce the sol or solution of the polymorphic ceramic material into the compact by slowly introducing the liquid into the vacuum vessel containing the compact. For example, the compact may be gradually submerged in the sol. When the compact is submerged, the vacuum may be increased and the samples "soaked" for a period of time, for example, for 10 to 15 minutes, to ensure good infiltration. Alternatively, the compact may be lowered into a sol or solution already present in the vacuum vessel.

Infiltration may also be accomplished without a vacuum, using a wicking process. In ceramics, wicking of a fluid into a porous compact may occur as a result of pore pressure. The pores act as capillaries which draw the fluid into the compact.

After infiltration, the compacts are then dried, for example, at temperatures of 110°C.

Heat Treatment

After infiltration and drying, as described above, the compacts are heat treated at temperatures in the range of from 25°C to 800°C, preferably at from 100°C to 700°C, and most preferably at 400°C, for from 1 to 24 hours to

remove volatile materials and to prepare the infiltrated compact for subsequent high heat sintering. To determine the minimum temperature needed to remove volatiles, the weight loss of the compact during heat treatment is monitored, using thermal analysis as shown in FIGURE 2. After heat treatment, the ceramic compact may then be weighed to measure mass gain, to determine the amount of zirconia infiltrated.

After all volatile compounds have been removed, and the samples weighed, the infiltrated compact is typically sintered to greater than 95% theoretical density to reduce pore size and increase strength and by heat treating at temperatures in the range of 800°C to 1700°C, preferably in the range of 1200°C to 1650°C, and most preferably at approximately 1650°C, for from 1 to 2 hours. The composites are then cooled to room temperature (25°C).

Repeated Infiltrations

For some applications, one cycle of infiltration as described above may be preferred, for example, where other parameters are varied, or where it is desirable to reduce manufacturing time and costs, or to reduce the weight of the final ceramic product. In other cases, infiltration may be repeated to increase the volume percent of zirconia until a desired amount of zirconia is introduced. To repeat infiltration, after infiltration as described above, the infiltrated compact is heat treated at temperatures between 25°C and 800°C, preferably between 100°C to 700°C, and most preferably at 400°C for from 1 to 24 hours to remove the volatiles as described above, until no further weight loss is discerned. The infiltrated compact is then cooled to room temperature and reinfiltrated as above, using a vacuum, eliminating the high heat sintering step until the final infiltration cycle, and then sintering at high temperatures, for example, at 1600°C.

When fabricating ceramic composites, using the infiltration process of the present invention, in order to obtain the toughness and strength of the composites produced, it is preferable to retain the zirconia in substantially tetragonal phase. By "substantially in tetragonal phase," it is meant that at least 10 volume percent of the zirconia within the microstructure in a given ceramic composite produced is in tetragonal phase. Most preferably, it is desired to maintain the volume percent of zirconia in tetragonal form at greater than 70 volume percent. Retention of zirconia in tetragonal form may be maximized by varying the porosity, pore size distribution, and pore-to-pore spacing of the porous compact, for example, by stabilizing the components of the suspension used to form the compact; or, by manually selecting the pore sizes and distribution, for example, by using the methods described in copending patent

application Serial No. 860,073, filed May 6, 1986, and assigned to the same assignee as the present application, the disclosure of which is incorporated by reference herein. In addition, the viscosity of the sol or solution used for infiltration may be varied, for example, to alter the amount of deposition of zirconia at various locations within the compact.

Measurement of Strength

The bend strength of the infiltrated ceramic composites, formed as described herein, may be determined using a standard strength measurement, such as the bending test as described by Baratta in Methods for Assessing the Structure Reliability of Brittle Materials, Eds. Freiman and Hudson, ASTM Special Technical Publication 844 (1982), incorporated by reference herein. Bending strength is defined as the maximum tensile strength of failure, and is often referred to as the "modulus of rupture." Bending strength may be expressed in units of kpsi (lb/in^2) x 10^3 or MPa (N/m^2) x 10^6, where "N" equals Newton and "m" equals meter. Bending strength may be characterized using a 3-point or 4-point bending load. In 3-point bending, the load is placed at the center of the test sample; whereas in 4-point bending, the load is placed at two positions on the sample, thus applying tensile stress over a range on the surface of the sample. In the example which follows, bend strength measurements were made on the infiltrated ceramic composites using 4-point bending, with a span of 23.2 mm in a load span of 13.2 mm. Load rate and chart speed were 0.5 mm/per minute and 20 mm/per minute, respectively. Each specimen was diamond-cut (3 x 5 x 25 mm cross section) and planed using a Struers Discoplan-TS (Struers, Inc., Cleveland, Ohio). The specimens were then surface-finished using a 45 micron diamond disc.

Determination of Fracture Toughness

In general, any increase in strength in a ceramic product which results from processing may be attributable to the elimination or partial elimination of surface defects (flaws), or may be a result of an increase in fracture toughness. However, if an increase in strength is accompanied by an increase in the fraction of zirconia retained in tetragonal phase, which may be determined using a procedure such as X-ray diffraction, then an increase in fracture toughness may be assumed.

The fracture toughness for ceramic composites containing different amounts of zirconia has been previously determined by measurements, of the stress intensity factor (Kc) of the ceramic. Kc may be measured using the indentation technique and the function: $Kc = \frac{H\sqrt{d}}{3(H/3E)} 4\, f(c/d)$, developed by Evans and Charles, J. Am. Ceram. Soc., 59, p.371-372 (1976), incorporated by

reference herein. Values for Kc have been measured and published for differing volume percents of zirconia (Lange, supra). Reference may be made to these values to illustrate the increase in toughness with increasing volume percent of zirconia over the complete range covered in this method. In lieu of direct measurements of toughness for a given volume percent of zirconia, assuming that the critical crack size distribution remains unchanged throughout a sample range, flexural strength may be taken as an indication of toughness using the relationship:

$$\sigma_2 = \frac{K_2}{K_1} \sigma_1$$

where σ_1 and σ_2 are the strengths of any two materials, and K_1 and K_2 are their respective stress-intensity factors.

Concentration Gradient

The accumulation of zirconia particles at various locations within the porous ceramic compact during the infiltration cycle will be a function of the initial concentration of the zirconia sol, its viscosity, the number of infiltration cycles, the depth of infiltration and the time over which infiltration occurs, as well as the volume of porosity and pore size distribution of the porous compact. One would thus expect to find concentration gradients, i.e., relative quantities of zirconia at different locations within the porous ceramic compacts which have been infiltrated. These concentration gradients are significant because they result in stress, density, and grain size gradients which, in turn, affect the physical (mechanical) properties of the ceramic bodies produced.

The following examples are presented to illustrate the present invention and to assist one of ordinary skill in making and using the same. The examples are not intended in any way to either limit the scope of the disclosure or the protection afforded by the grant of Letters Patent hereon.

EXAMPLE I

Preparation of Porous Compacts

Colloidal suspensions of 45 volume percent (v/o) (AKP 30) alpha alumina (Sumitomo Chemical America, Inc., New York, NY) in water were dispersed using steric stabilization with Darvan C and citric acid. The suspensions were filtered using a plaster batt made with a 75:25 weight ratio of plaster:water, and teflon mold walls of the desired shape to form "green" compacts. After consolidation, the compacts were dried at 110°C for 24 hours, and partially sintered at 1100°C for 1 hour (after heating the samples up to that temperature over four hours time) to form porous ceramic compacts with sufficient strength to withstand infiltration, as described below. Upon cooling,

the compacts were shaped using a 180 grit wet sander and cut to form cakes (40 mm x 10 mm x 60 mm). After shaping, the compacts were dried at 110°C for 24 hours, followed by density measurements using the Archimedes displacement technique.

EXAMPLE II

Infiltration of Porous Compacts

For infiltration, sols of acetate-stabilized zirconia (Remet Corp., Chadwicks, New York) were used containing 20 volume percent zirconia. Two sols with viscosities of 10 centipoise (cp) and 75 cp, marked 1985 and 1982, respectively, were prepared. Zirconia particle size in both sols was 20 $\overset{o}{A}$ as determined from the micrograph of FIGURE 1. Both sols were treated in the same manner throughout the examples.

The porous alumina compacts prepared as described above were placed in a vacuum chamber and a vacuum of 1.5×10^{-2} torr was drawn and maintained for 20 minutes, at which time the vacuum was reduced to 50 torr. One of each of the above sols was then introduced into the chamber via a stopcock at a rate of approximately 1 drop per second until the sample was fully submerged. The vacuum was then increased to 1.5×10^{-2} torr, and the samples were soaked for a period of 20 minutes to ensure good infiltration. After soaking, the samples were removed and placed directly in a drying oven at 110°C for 9 hours, followed by heat treatment at approximately 876°C for 9 more hours. Samples infiltrated by both sols (1985 and 1982) were then weighed to determine mass gain during infiltration. Following infiltration, the samples were sintered at temperatures between 1200°C and 1700°C to achieve densification and strength.

EXAMPLE III

The procedures of Examples I and II were employed to produce a ceramic composite repeatedly infiltrated with zirconia (one to ten cycles). After the initial soak for one cycle of infiltration (Example II), the sample was heat treated at 400°C until no further weight loss was observed (as measured by thermal analysis, see FIGURE 2), followed by cooling to room temperature and reinfiltrating using the procedure described in Example II. The samples were sintered after all infiltration cycles were completed. FIGURE 3 gives the increase in volume percent of zirconia, based on total volume as a function of infiltration frequency for the 10 cp and 75 cp sols. The volume percent zirconia was determined by weighing the samples to measure the "before" and "after" infiltration masses, and using the known densities of zirconia and alumina. The higher viscosity zirconia sol (75 cp) showed a decrease in zirconia deposition

after 10 infiltration cycles, while the 10 cp sol still showed fairly large increases in deposition. The decrease in deposition of the higher viscosity sol may be due to decreased penetration of the sol.

As shown in Table I above, increased zirconia content in an alumina zirconia composite leads to a decrease in metastable tetragonal grain size. Grain growth of zirconia inclusions occurs by alumina grain boundary movement, hence high zirconia content should result in larger zirconia grains with a corresponding decrease in retained tetragonal phase. FIGURE 4 illustrates this behavior for a number of infiltration cycles. FIGURES 4 and 5 show that for 1 infiltration of the 10 cp sol, 100% tetragonal zirconia grains were retained up to a temperature of 1600°C. For increasing numbers of infiltration cycles (4, 6), the fraction of tetragonal zirconia decreases with increasing densification.

EXAMPLE IV

Effects of Reinfiltration on Densification

The composites infiltrated according to Examples I through III were sintered at various temperatures following heat treatment to determine the effects of the number of infiltration cycles on densification. Thus, samples selected from the composites infiltrated with zirconia for one to ten cycles were sintered after heat treatment at temperatures of 1300°, 1400°, 1500° or 1600° C for one hour. FIGURE 5 depicts the effects on sintering density (expressed as a percentage of theoretical density) of the different sintering temperatures for 1, 4 and 6 infiltration cycles. Sintering at 1600°C for 4 and 6 infiltration cycles produced 95% theoretical density. For lower infiltration frequency, sintering is initially retarded in the alumina matrix, but after densification is initiated, sintering is rapid. For increasing amounts of zirconia infiltrated into the alumina matrix, increased densification is not seen at any of the tested sintering temperatures.

EXAMPLE V

Effects of Isothermal Sintering

Infiltrated ceramic composites, obtained as described above in Examples I through III, were selected for a number of infiltrations (1-10) and subjected to isothermal sintering at 1500°C for from one to seven hours to study the effects of isothermal sintering on the percentage of zirconia retained in tetragonal form, i.e., the effect of grain boundary movement on zirconia particle inclusion size. The results are shown in FIGURE 6, depicting isothermal sintering effects on the fraction of tetragonal zirconia retained. As the number of infiltrations increases, the fraction of zirconia retained in tetragonal phase

decreases due to coalesence of zirconia particles from grain boundary move-
ment. Therefore, sintering time and temperature should be maximized with
respect to density, and the fraction of tetragonal zirconia retained.

From Examples IV and V it can be seen that a maximization of
strength and toughness, using a low volume percent of zirconia content, is
desirable both to increase the efficiency of processing and to maximize
tetragonal polymorph retention. Achieving a low zirconia content does not
require a high number of re-infiltrations or high sintering temperatures, and
decreasing the number of infiltrations increases tetragonal zirconia retention.

EXAMPLE VI

Determination of Zirconia Concentration Gradient

To determine the concentration gradients of the zirconia in-
filtrated into the porous compacts, cross sections were made of composite
samples prepared with a number of infiltration cycles (1-10) of a similar size to
composites prepared for mechanical strength tests. Energy Dispersive X-Ray
Analysis (EDAX) readings were taken at varying depths from the surface of
composites for varying infiltration cycles. The integrated intensities of
aluminum and zirconium peaks were then compared for the various positions in
the samples to determine the corresponding relative concentration gradients.

FIGURE 7 provides, in graph form, the EDAX concentration
gradients showing the relative amounts of zirconium (metal) at various locations
(depths) within the composite body. This graph shows (suggests) that more
zirconium is present at the surface of the composites with a fairly rapid
decrease in concentration moving away from the surface (e.g., .25 mm) for the
10 cp and 75 cp sols for 2, 6, and 10 infiltration cycles. This graph also suggests
that, in higher viscosity zirconia sols, a larger gradient near the surface of the
composite results and thus the relative amount of zirconia incorporated in the
surface of the composite may be increased by using higher viscosity sols.

Differing concentrations of zirconia result in a range of the size of
the alumina matrix grains. Thus, low concentrations of zirconia result in a large
distribution of matrix grain size, while large concentrations of zirconia will
correspond to matrix grains with a narrow distribution of sizes. This concentra-
tion-size effect is seen in the cross section of one composite shown in
FIGURE 8a, where the outside edges have a higher concentration of zirconia
than the interior. FIGURES 8a-e compare the grain size distribution seen in
composite samples. Note the number of intragranular zirconia inclusions
corresponding to low concentrations, as compared to the great proportion of
grain boundary-junction inclusions in the high zirconia concentration areas.

The microstructures seen in FIGURES 8a-e are the result of concentration gradients within ceramic composites infiltrated with zirconia for 3 and 10 infiltration cycles at 1600°C, using the 75 cp zirconia suspension (FIGURES 8a, b), for 6 infiltrations of the 10 cp suspension at 1500°C (FIGURE 8c), and for 3 infiltrations of the 75 cp suspension at 1400°C (FIGURE 8d), as compared to pure alumina (FIGURE 8e). The concentration gradients of zirconia are expressed as relative quantities as a function of depth obtained from the EDAX readings on a cross section of the sample.

EXAMPLE VII

Determination of the Strength of Infiltrated Ceramic Composites

Mechanical strength tests were run in a conventional manner on sintered compacts, as desribed above, and infiltrated with either the 1982 or 1985 zirconia suspension, as described in Examples I and II, to study the effects of viscosity of the zirconia suspension on strength. Samples infiltrated 10 times with the 1982 suspension (viscosity 75 cp) were sintered to 1600°C over a 13 hour period, followed by a soak period of 1 hour. Samples infiltrated 6 times with the 1985 suspension (viscosity 10 cp) were heated to 1600°C for a period of 6 hours, followed by a 1 hour soak and then cooling for 5 hours. Both samples were cut in half (sample size now 3 x 5 x 27 mm) and planed using a Struers 15 micron planer. A 45 micron diamond disc was used to surface finish the samples. Surface finishing may cause transformation of tetragonal zirconia to the monoclinic form creating compressive stresses, resulting in higher strength values. The bend strength of the composites was measured using 4-point bending tests (inner span of 23.2mm, load span of 13.2mm) using a load rate of 0.5mm/min., and chart speed of 20mm/min., respectively.

Strengths on the order of 750 MPa were obtained with a mean strength of 677 MPa for 6 infiltrations with the 10 cp suspension. Strengths of 650 MPa, with a mean of 580 MPa, were obtained for 10 infiltrations with the 75 cp suspension. Since the ratio of zirconia concentration at the surface, when comparing samples produced using the 10 cp and 25 cp suspensions, was 0.9:0.65, while the volume fraction of tetragonal zirconia for both samples was 40%, the strength differences in the samples may be attributable to this large variation in retained tetragonal phase at the surface.

These strength values, in light of the increased fraction of zirconia retained in tetragonal phase in the surface of the samples, indicate enhanced surface toughness of the composite samples over those of pure alumina.

EXAMPLE VIII

Determination of Fracture Toughness of Infiltrated

Ceramic Composites

Indentation tests are run, as described by Evans and Charles, supra on samples infiltrated with the 1985 zirconia suspension. Samples are infiltrated 1, 2, 3, 5 and 6 times, as described above. The distribution of zirconia within the composites illustrated in FIGURE 7 suggests that measurable values of surface toughness should follow a similar gradient. Therefore measurements are made of the cross-sections and surfaces of the samples.

EXAMPLE IX

Effect of Pore Size Variation on Strength of Infiltrated Ceramic Composites

To determine the effects of pore size variation on the strength of ceramics, infiltrated colloidal suspensions of 55 v/o alpha alumina are used to form porous compacts as described above in Example I. The porous compacts are then partially sintered, using a range of temperatures, to produce porous compacts with a range of pore sizes prior to infiltration. The compacts are then dried at 100°C for 24 hours.

The porous compacts are then partially sintered at 1100°C, 1200°C, 1300°C or 1350°C, for 60 minutes at each temperature (temperatures are raised at a rate of 15 degrees/min.). Sintering at these temperatures has been found to produce a range of pore sizes of from 0.075 to 0.04 μm for 55 volume/percent alpha alumina powder containing particles of .35 μm diameter. Han, supra. Because the partial sintering steps used by Han were similar, Han's data can be used to approximate the pore sizes obtained in the porous compacts produced herein.

The partially sintered, porous compacts are infiltrated with a 10 cp zirconia sol prepared as described above in Example II. The compacts are then repeatedly infiltrated, as described above in Example III, for 0, 1, 2, and 3 cycles. The infiltrated compacts are then dried at 110°C for 12 hours, heat treated at 600°C for 1 hour, and weighed to determine mass gain. The compacts are then sintered at 1650°C, raising the temperature at a rate of 15 degrees/minute, for 60 minutes. Strength and toughness measurements, as described above in Example VII, are then made on the sintered, infiltrated ceramic bodies.

The results of the above examples demonstrate that by using the process of the present invention, surface toughened ceramic composites may be obtained by infiltrating a porous ceramic body with a sol or solution of zirconia. The properties of the ceramic composites produced may be optimized by varying

the number of infiltrations and viscosity of the infiltration sol. The volume of porosity and pore size distribution of the ceramic compacts may also be varied by partially sintering the porous compacts before infiltration. Although unstabilized zirconia was described in the examples, stabilized sols or solutions may be used to infiltrate porous ceramics. Stabilized sols or solutions may increase the fraction of zirconia which can be retained in tetragonal phase with increasing volume percents of zirconia.

While the present invention has been described in conjunction with preferred embodiments, one of ordinary skill after reading the foregoing specification will be able to effect various changes, substitutions of equivalents, and alterations to the compositions and methods set forth herein. It is therefore intended that the protection granted by Letters Patent hereon be limited only by the appended claims and equivalents thereof.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1.   A method for preparing a surface toughened ceramic body comprising:

(a)   infiltrating a porous ceramic compact with a ceramic material to form an infiltrated compact; and

(b)   heating said infiltrated compact to form a high-strength, infiltrated ceramic composite.

2.   The method according to Claim 1, wherein said ceramic material is a polymorphic material.

3.   The method according to Claim 2, wherein said polymorphic ceramic material is stabilized zirconium oxide.

4.   The method according to Claim 2, wherein said polymorphic material is unstabilized zirconium oxide.

5.   The method according to Claim 1, wherein said step of infiltrating comprises infiltrating using a sol comprising submicron zirconium oxide particles.

6.   The method according to Claim 5, wherein the viscosity of said zirconium oxide sol is in the range of 5 to 100 centipoise.

7.   The method according to Claim 5, wherein the viscosity of said zirconium oxide sol is 10 centipoise.

8.   The method according to Claim 5, wherein the viscosity of said zirconium oxide sol is 75 centipoise.

9.   The method according to Claim 3, wherein said zirconium oxide is in solution.

10.   The method according to Claim 1, wherein said porous ceramic compact is fabricated from a member selected from the group consisting of alpha alumina, beta alumina, silica, titania oxides and mixtures thereof.

11.   The method according to Claim 1, wherein said step of infiltrating comprises repeating infiltration for from 1 to 10 cycles.

12.   The method according to Claim 1, wherein said step of infiltrating comprises infiltrating using a polymeric solution containing zirconium oxide.

13.   The method according to Claim 12, wherein said polymeric solution comprises zirconium oxide alkoxide.

14.   The method according to Claim 1, wherein said porous ceramic compact is unsintered.

15.   The method according to Claim 1, wherein said porous ceramic compact is sintered prior to said step of infiltrating.

16.   The method according to Claim 1, wherein said step of heating comprises the substeps of heat treating said infiltrated compact to remove volatile components and then sintering said heat treated compact to form a high-strength, infiltrated ceramic composite.

17.   The method according to Claim 16, wherein said heat treating substep comprises heating said infiltrated compact to temperatures from 25°C to 800°C for from 1 to 24 hours.

18.   The method according to Claim 17, wherein said heat treating substep comprises heating said infiltrated compact to temperatures from 100°C to 700°C.

19.   The method according to Claim 16, wherein said heat treating step is repeated until no further weight loss of the porous compact is achieved.

20.   The method according to Claim 19, wherein said heat treating step comprises heating said compact to a temperature of approximately 400°C.

21.   The method according to Claim 16, wherein said sintering substep comprises heating said heat treated infiltrated compact to temperatures from 800°C to 1700°C for from 2 to 20 hours.

22.   The method according to Claim 16, wherein said sintering substep comprises heating said heat treated infiltrated compact to approximately 1650°C.

23.   The method according to Claim 5, wherein said step of infiltrating comprises introducing said sol into said porous compact under vacuum.

24.   The method according to Claim 23, wherein said step of introducing said sol comprises:
        (a)   placing said porous ceramic compact in a vacuum;
        (b)   introducing said sol into said vacuum so as to submerge the porous ceramic compact in said sol; and
        (c)   soaking said porous ceramic compact in the sol to infiltrate said compact.

25.   The method according to Claim 1, wherein said step of infiltrating comprises introducing said ceramic material into said compact using pore pressure.

26.   The method according to Claim 23 or 25, wherein said step of infiltrating is repeated to increase the amount of ceramic material in said porous compact.

27.   The method according to Claim 26, wherein said step of infiltrating comprises from 1 to 10 cycles.

28.   The method according to Claim 1, wherein said porous ceramic compact is partially sintered prior to said step of infiltrating.

29.   The method according to Claim 28, wherein said porous ceramic compact is partially sintered at temperatures in the range of 800°C to 1400°C.

30.   The method according to Claim 28, wherein said porous compact is partially sintered at approximately 1100°C.

31.   A surface-toughened, infiltrated ceramic composite produced by the method according to Claim 1.

32.   A surface-toughened, infiltrated ceramic composite produced by the method according to Claim 26.

33.   The composite according to Claim 31 or 32, wherein said composite is infiltrated with zirconium oxide.

34.   A surface-toughened ceramic composite comprising from 1 to 15 volume percent zirconium oxide (ZrO_2) in the form of crystalline grains of substantially tetragonal structure having a diameter of less than 2 μm, the remainder of said ceramic composite being substantially aluminum oxide (Al_2O_3).

35.   The ceramic according to Claim 34, wherein the fraction of zirconium oxide in tetragonal structure is from 10 percent to 100 percent.
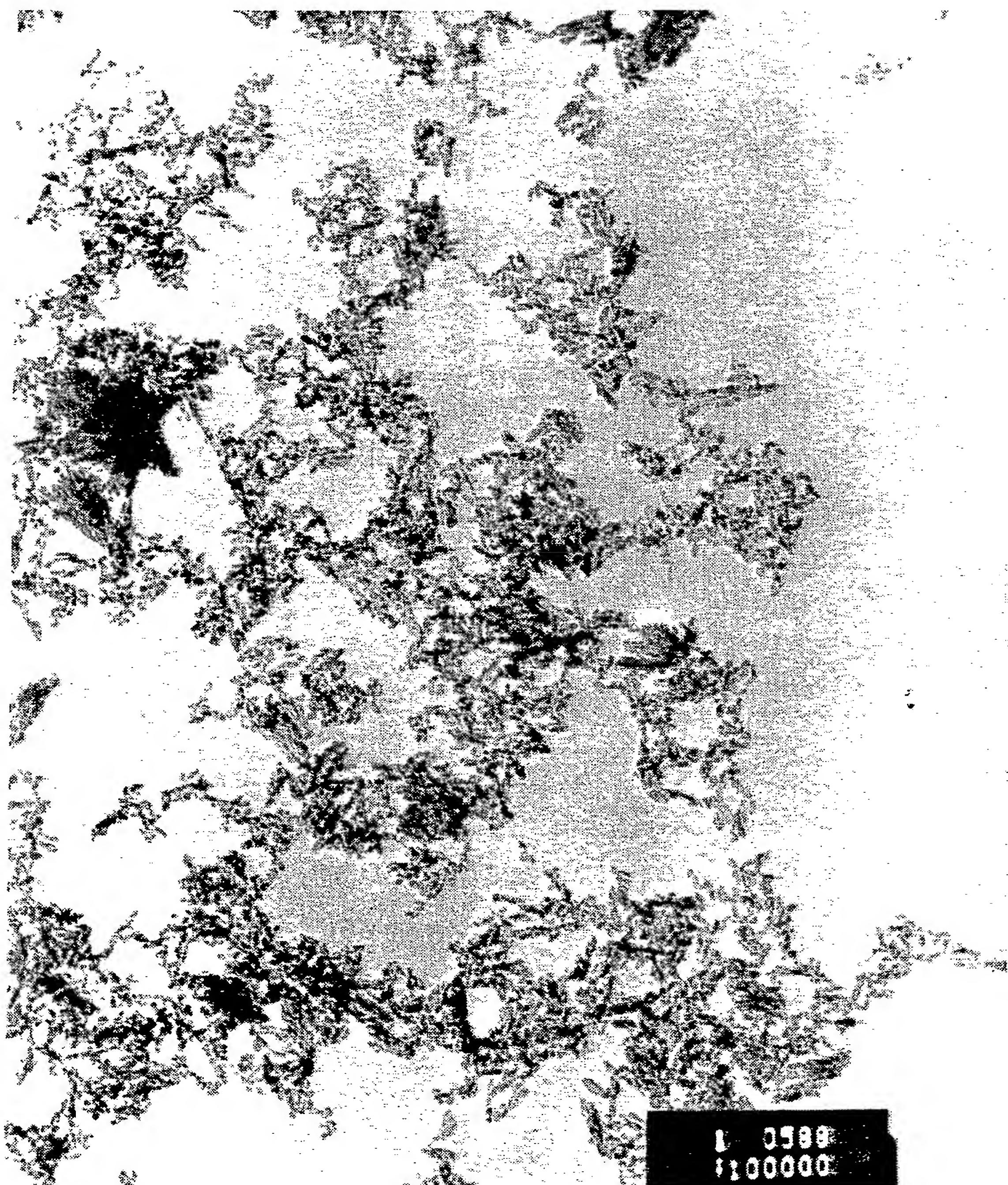
Fig. 1.

Fig. 2.

fig.3.

INFILTRATION FREQUENCY VS V/O ZIRCONIA

• 1985 SUSPENSION 10 CP
▲ 1982 SUSPENSION 75CP

INFILTRATIONS

V/O ZIRCONIA

Fig. 4.

TETRAGONAL FRACTION OF ZIRCONIA VS % DENSITY

% TETRAGONAL

% THEORETICAL DENSITY

▲ 1 INFILTRATION 10 cP
□ 4 INFILTRATIONS 10 cP
■ 6 INFILTRATIONS 10 cP

Fig.5.

SINTERING DENSITIES

% THEORETICAL DENSITY

TEMP C (1 HOUR)

△ PURE ALUMINA
▲ 1 INFILTRATION 10 CP
□ 4 INFILTRATIONS 10 CP
■ 6 INFILTRATIONS 10 CP

100
90
85
70
60
50

1100   1200   1300   1400   1500

Fig. C.

TETRAGONAL FRACTION ZIRCONIA ISOTHERMAL SINTERING

% TETRAGONAL

HOURS AT 1500 C

▲ 1 INFILTRATION 10 CP
□ 4 INFILTRATIONS 10 CP
■ 6 INFILTRATIONS 10 CP

EDAX CONCENTRATION GRADIENTS

Δ 6 INFILTRATIONS 10 CP
□ 2 INFILTRATIONS 10 CP
○ 10 INFILTRATIONS 75 CP

Fig. 7

Fig. 8B.

Fig. 8A.

2μ

Fig. 8D.

2μ

Fig. 8C.

2μ

Fig. 8F.

2μ

Fig. 8E.

2μ ⎯

Fig.8H.



2μ ⎯

Fig.8G.
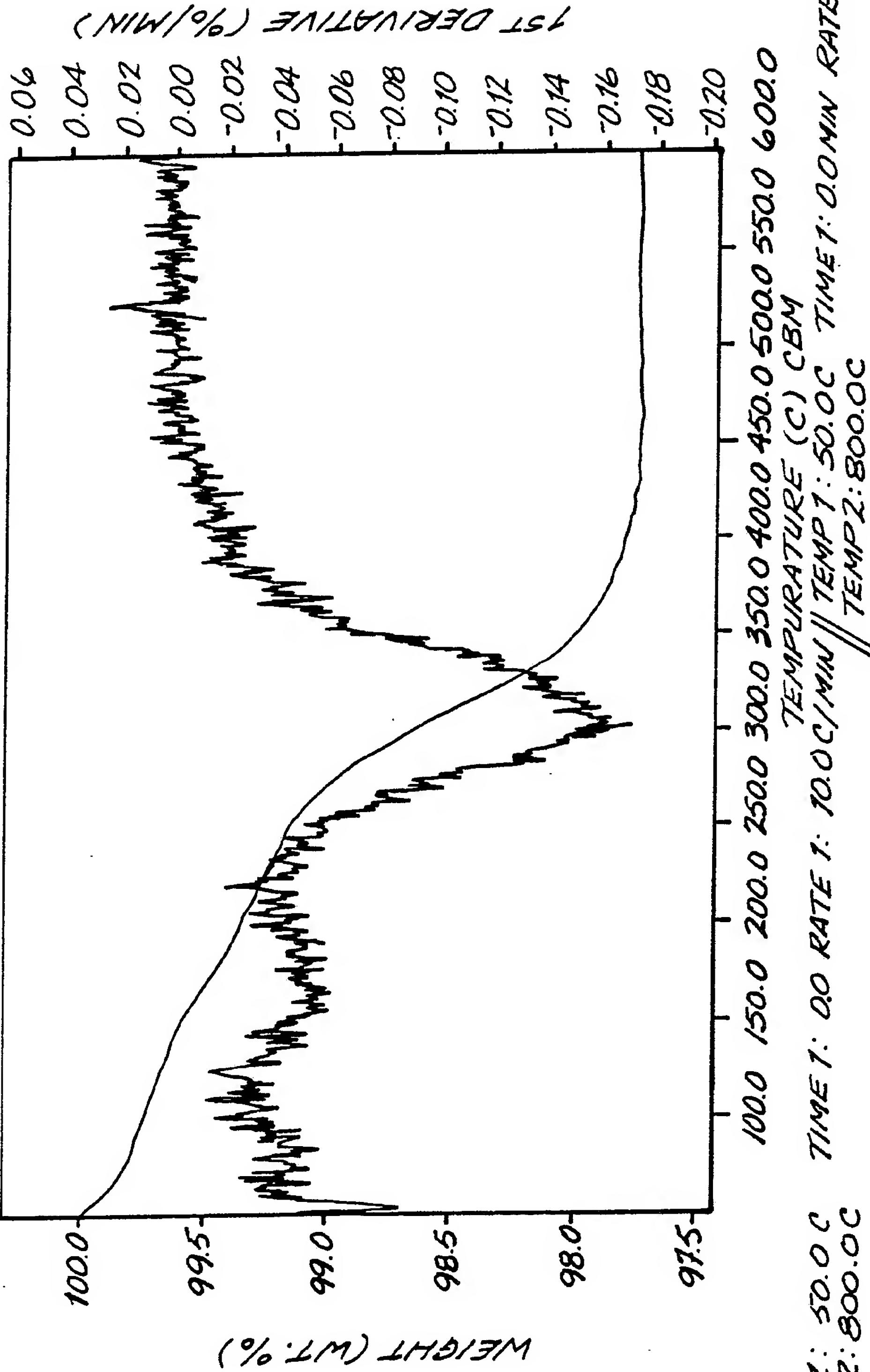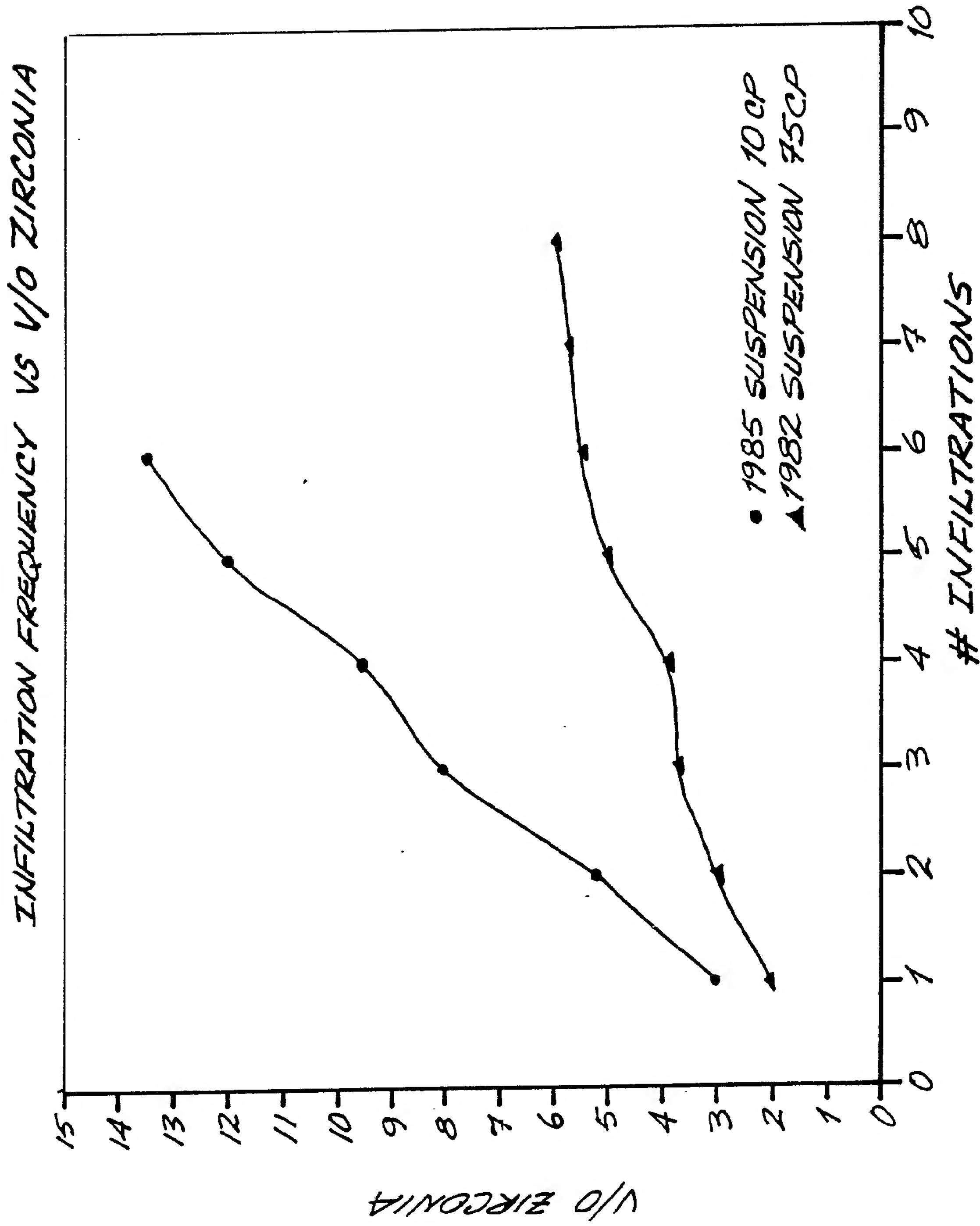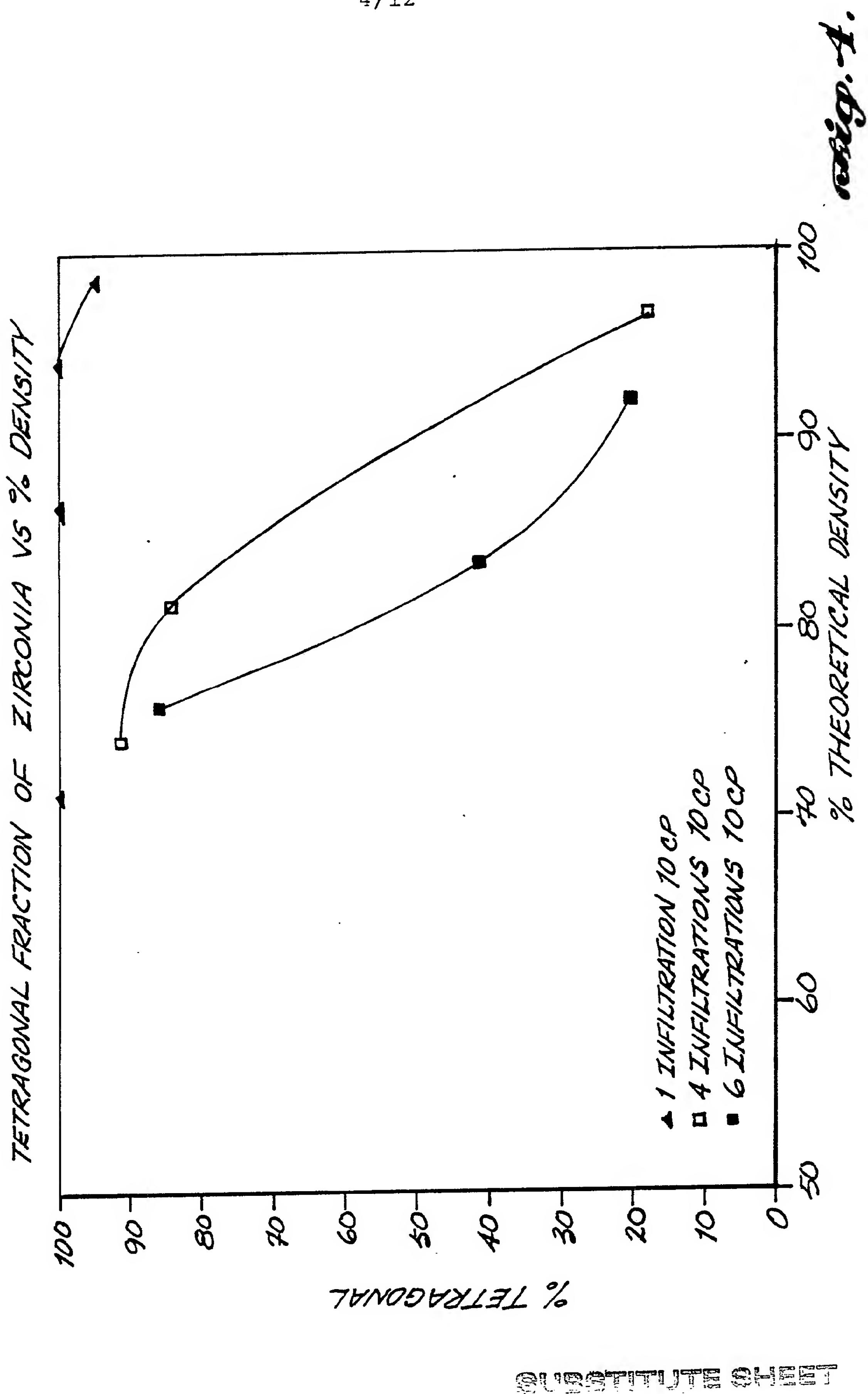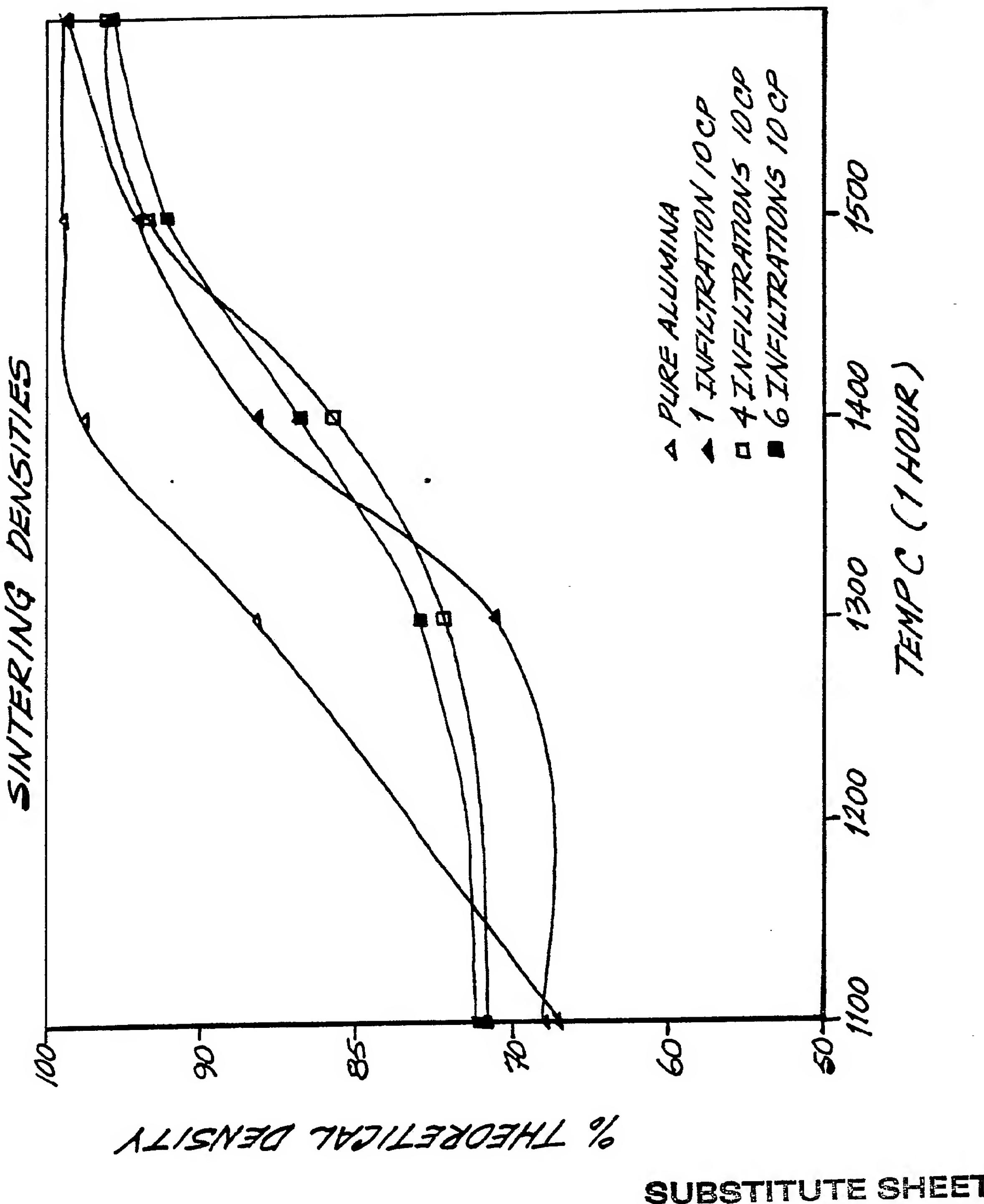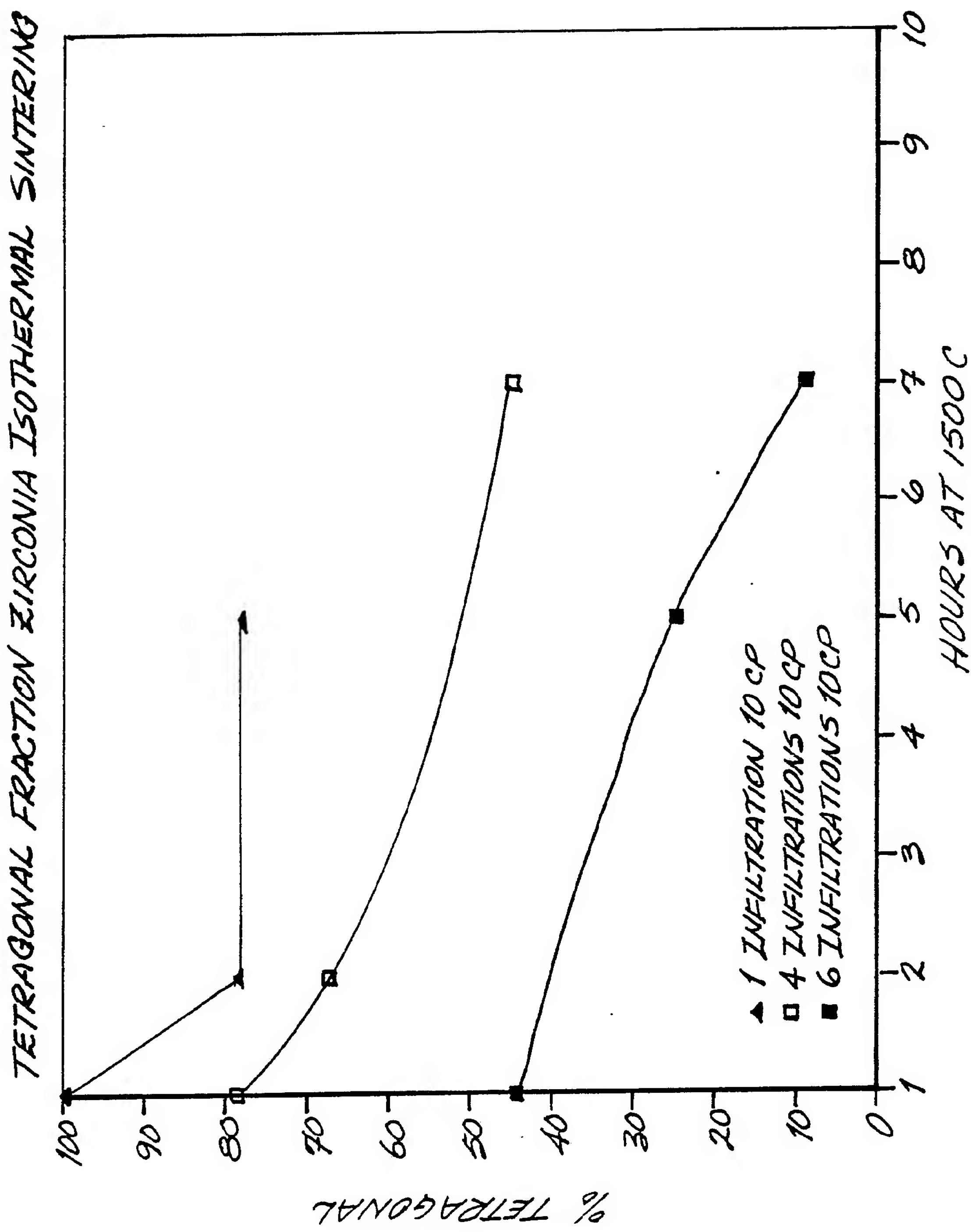
Fig. 18.

Fig. 18.
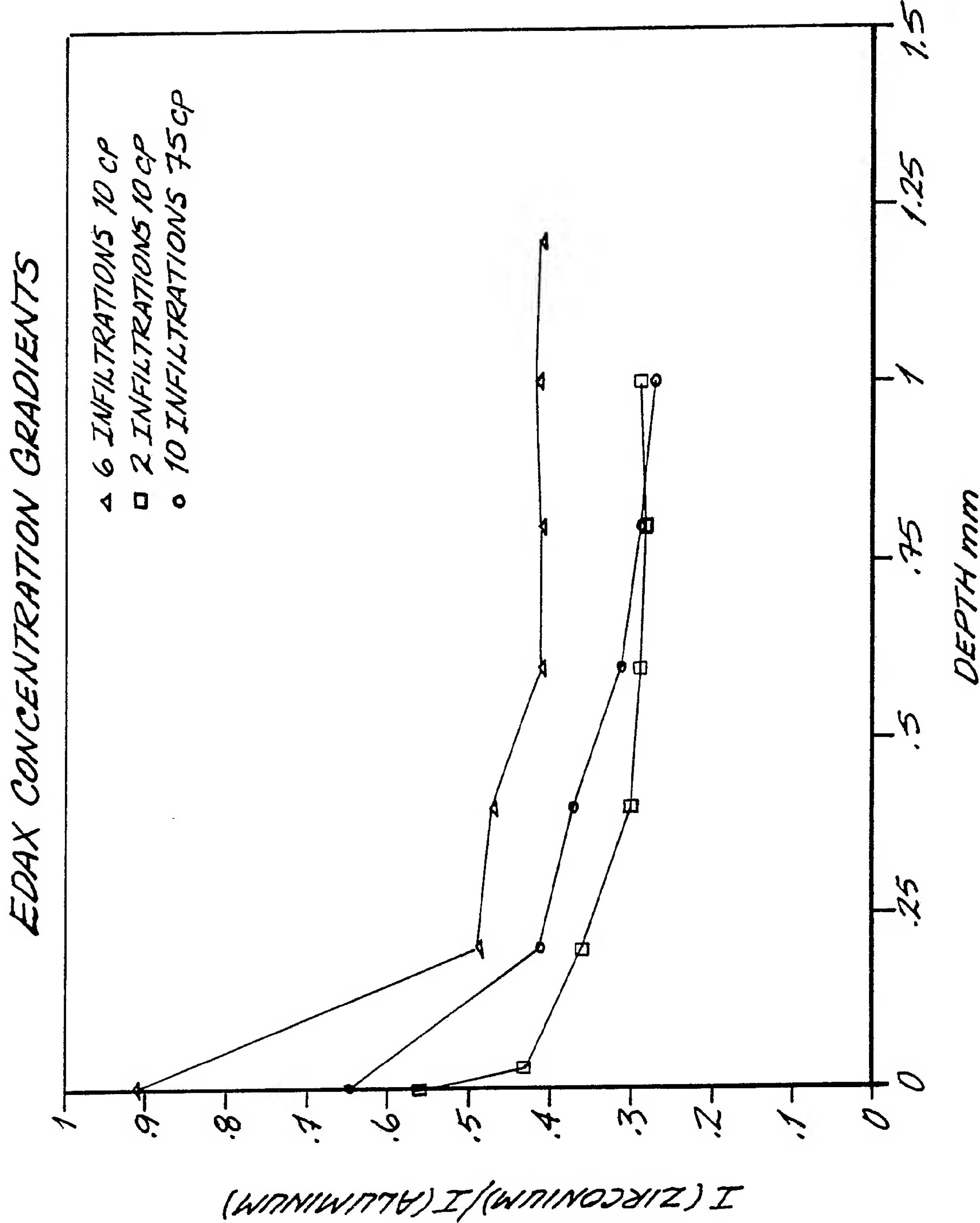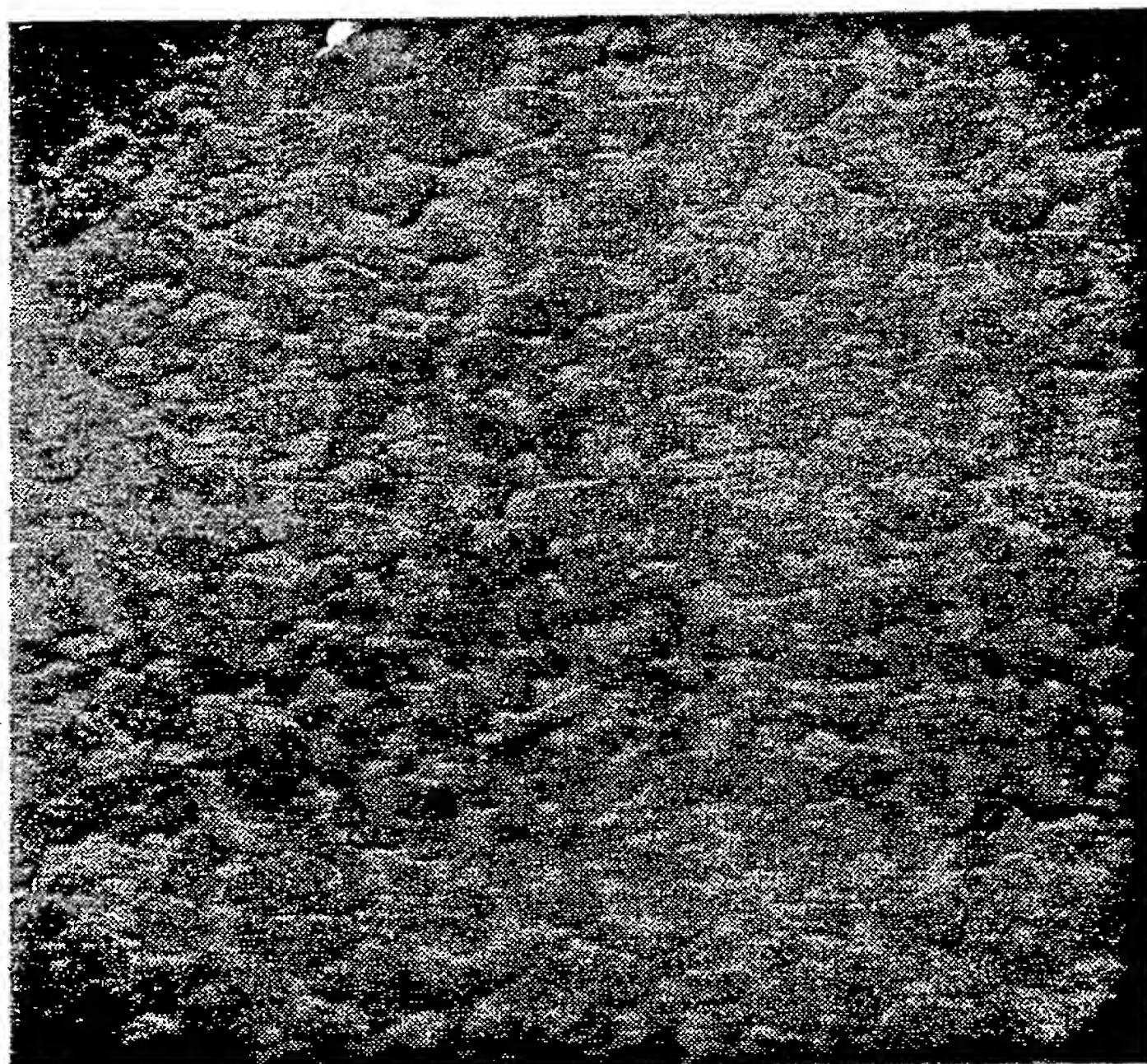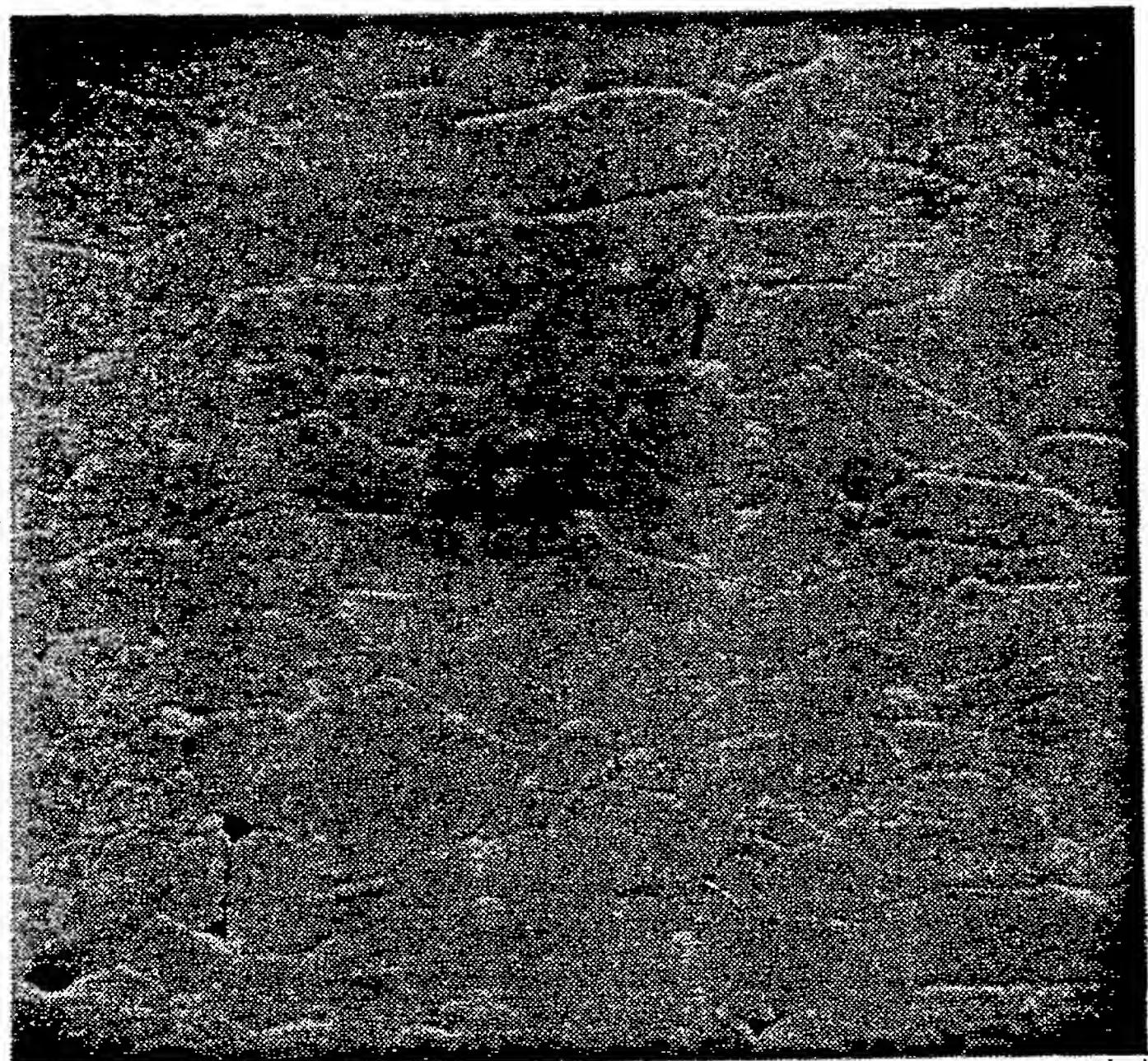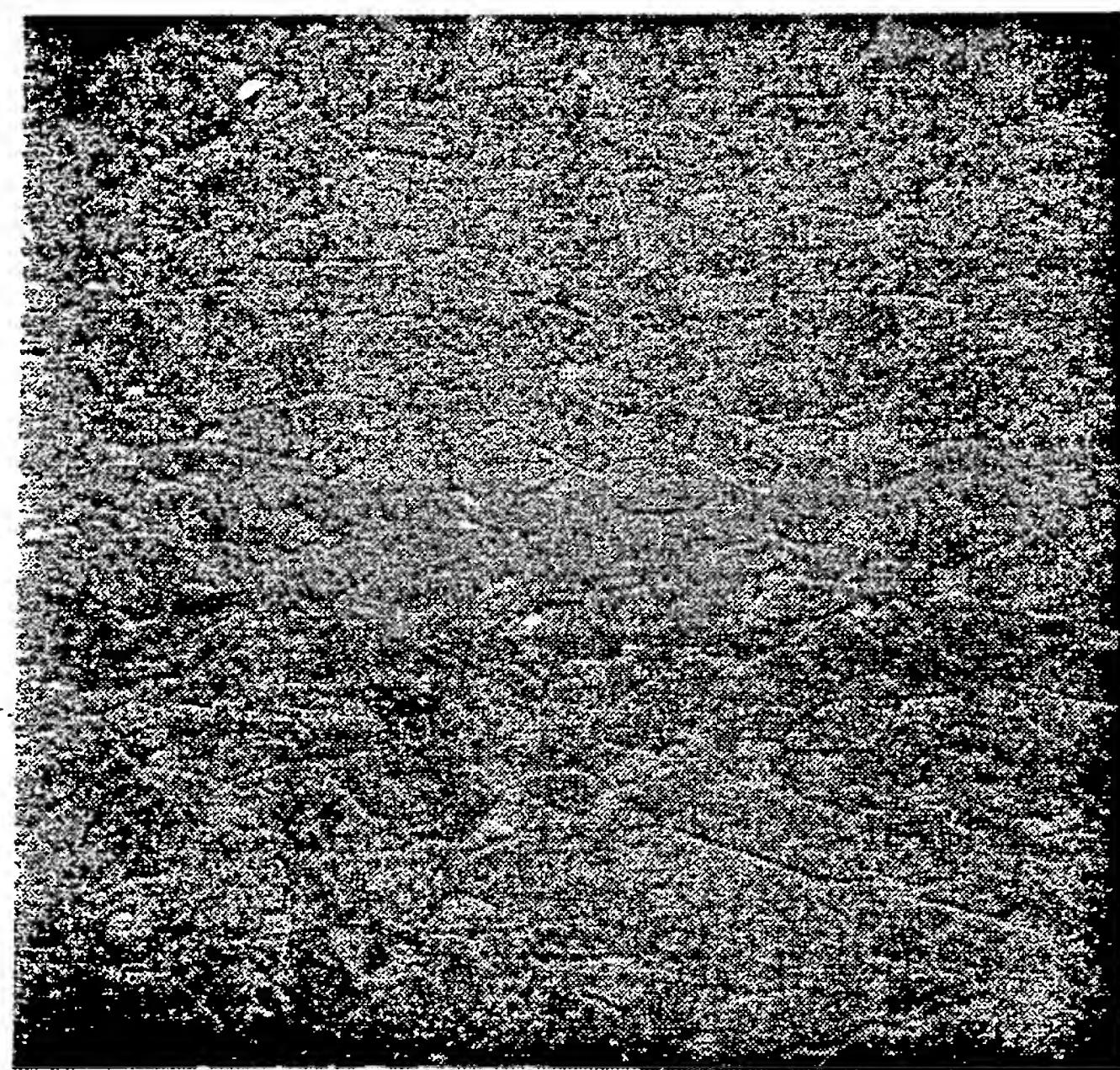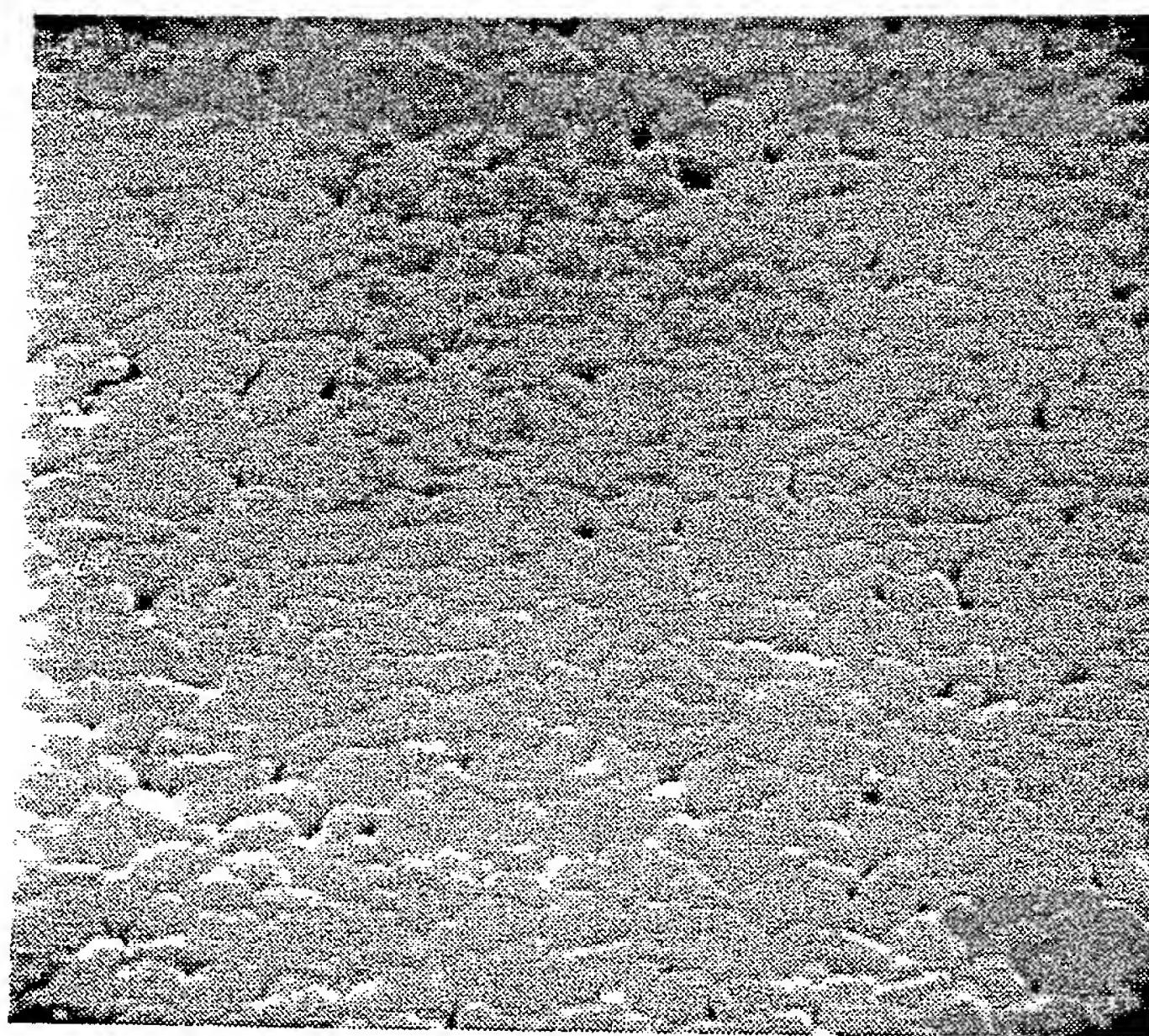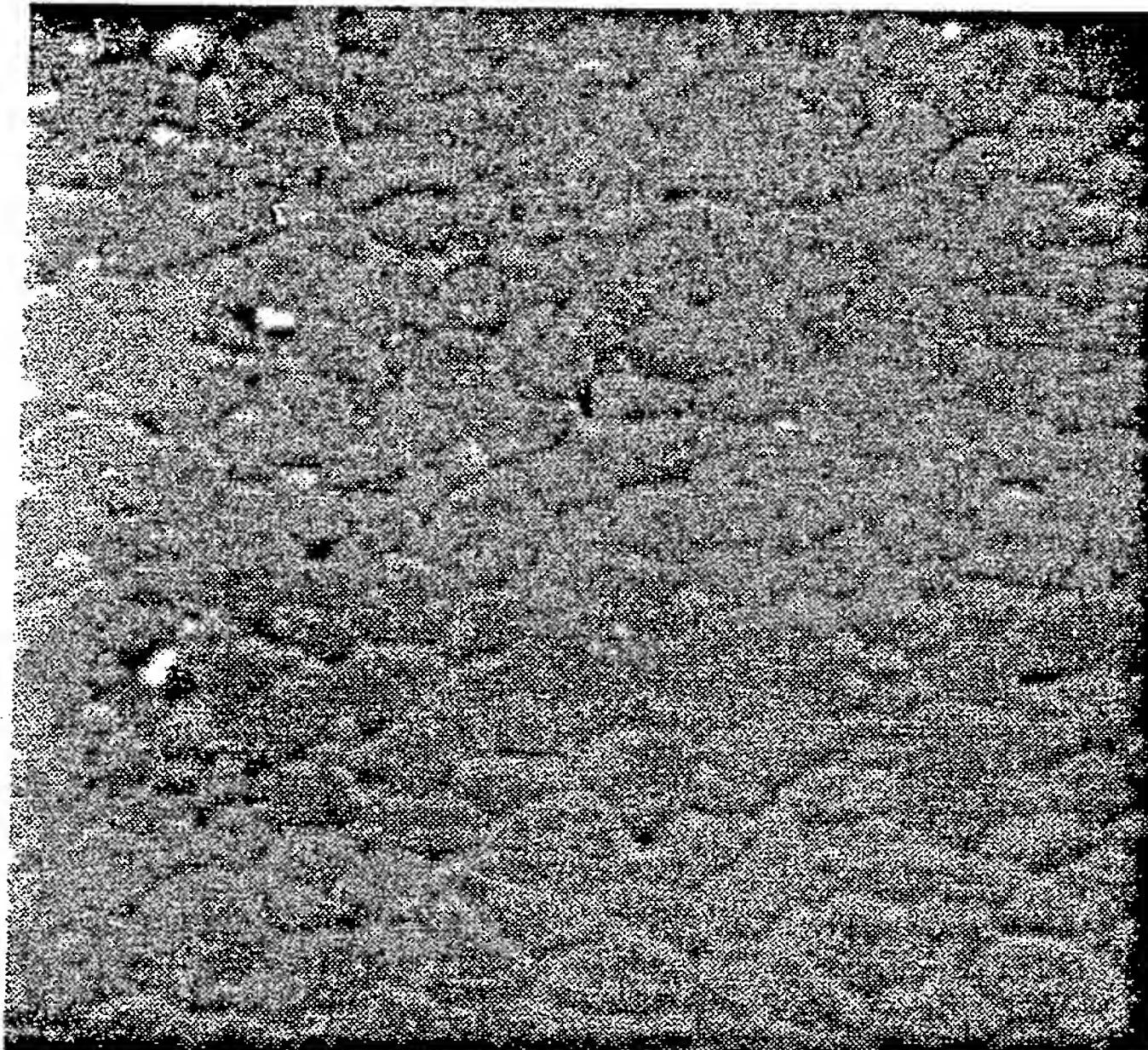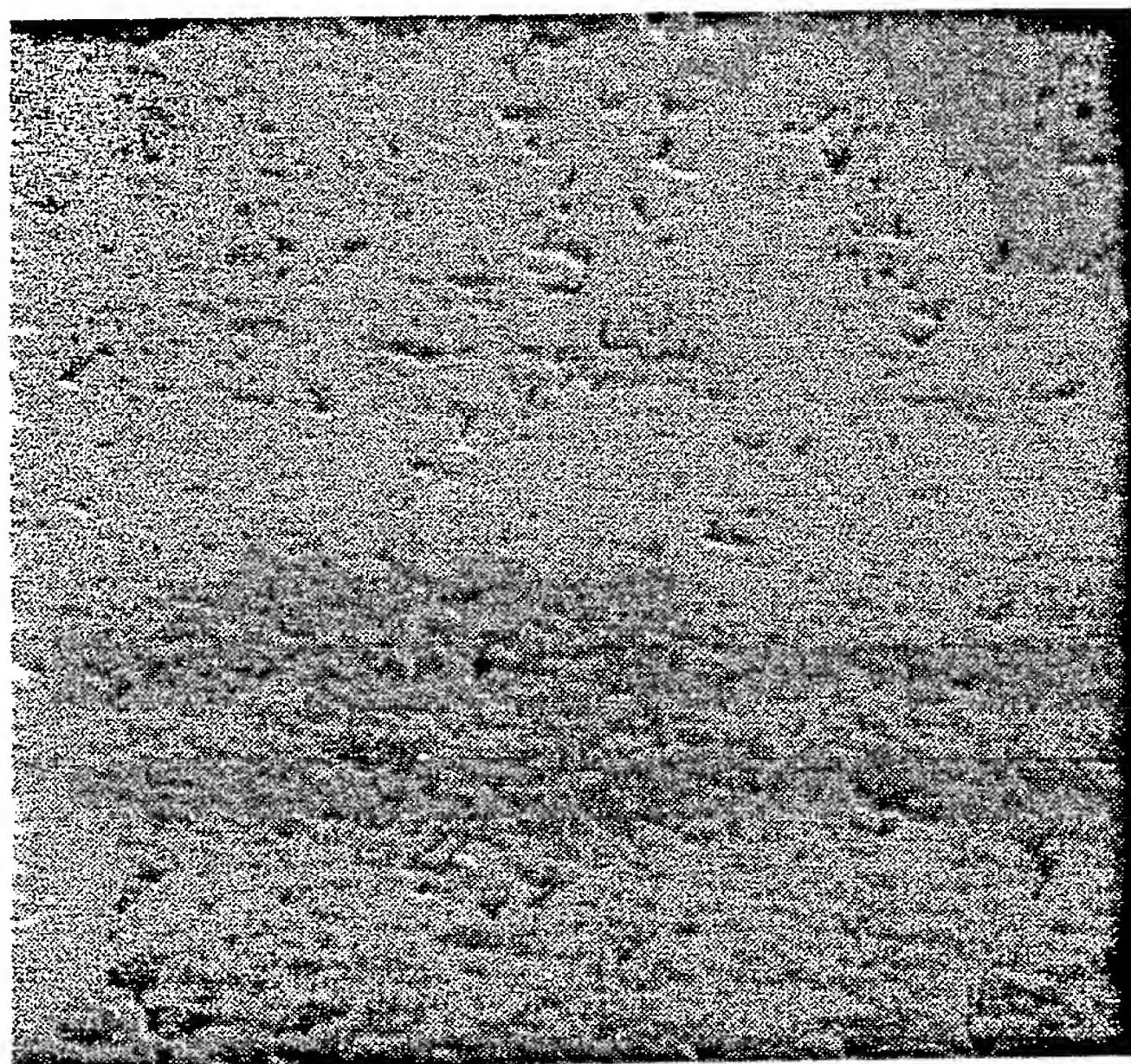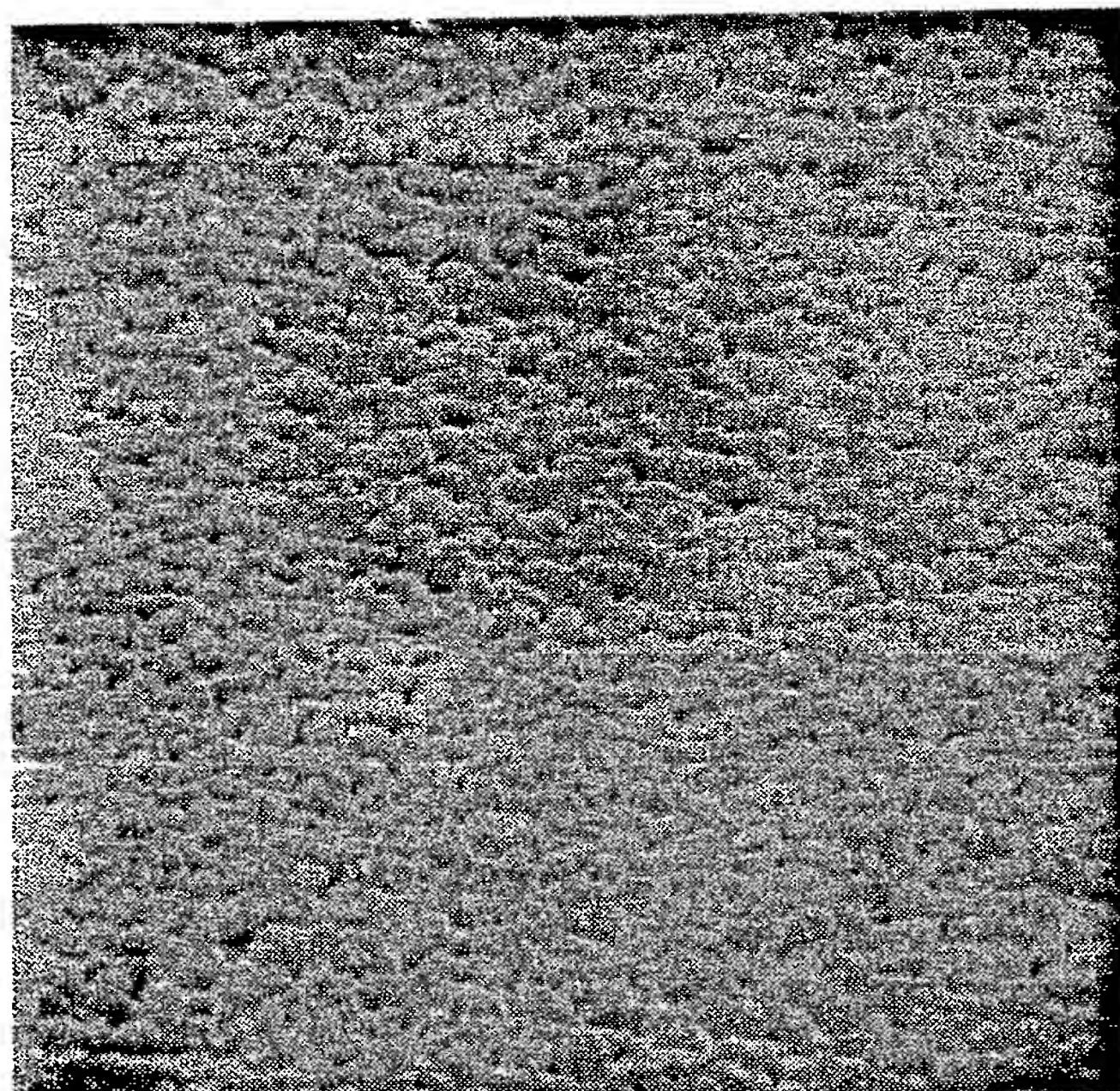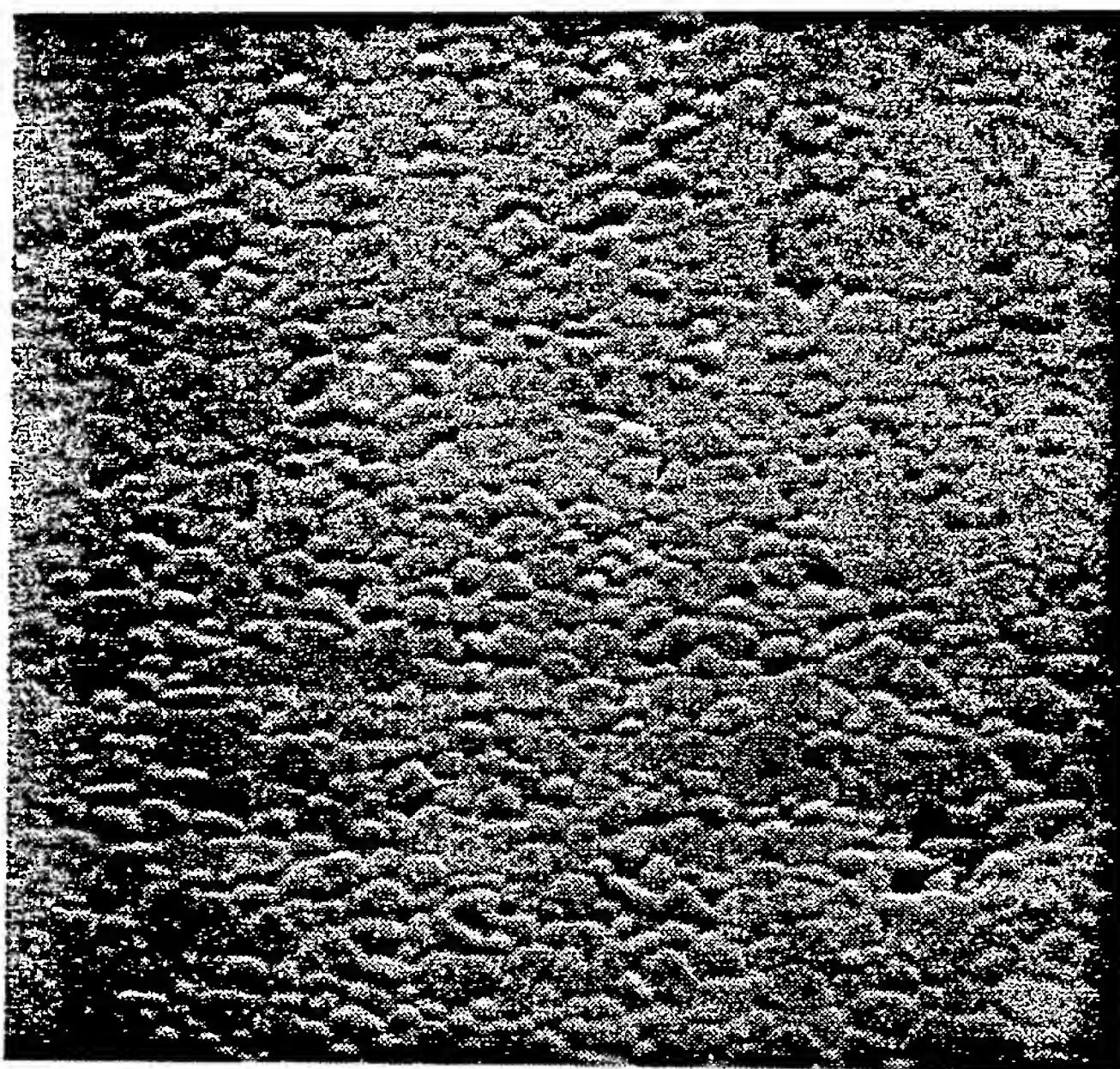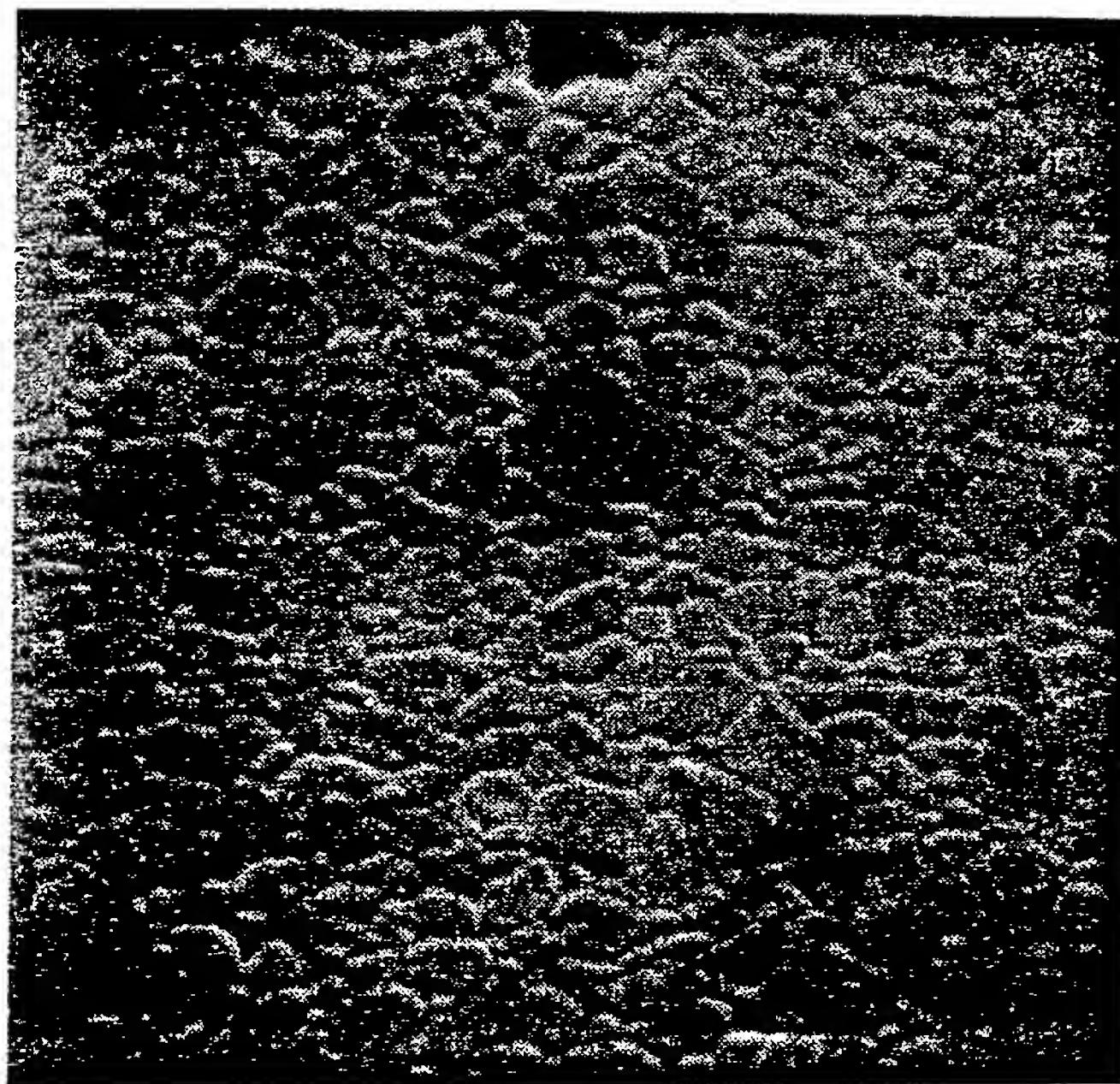
INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/02490

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁴: C 04 B 41/87, C 04 B 35/10

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
IPC⁴	C 04 B 41/00; C 04 B 35/00

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category*	Citation of Document,¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 4316964 (F.F. LANGE) 23 February 1982, see abstract cited in the application	1-3,10,11, 31,33-35
Y	US, A, 4358486 (G.M. ECORD et al.) 9 November 1982, see abstract; claims	1-3,10,11, 31,33-35
A	FR, A, 2230603 (KAMAN SCIENCES CORP.) 20 December 1974, see claims 1,2,5	1,31
A	DE, C, 666698 (R. REICHMANN et al.) 26 October 1938, see claim 1	1,14
A	CH, A, 456429 (ÖSPAG) 31 July 1968, see claims	1,11,15,23, 24,26,31-33
A	BE, A, 840132 (CENTRE DE RECHERCHES METALLURGIQUES) 16 July 1976, see claims 1,5	
A	LU, A, 56944 (D.J. NELL et al.) 23 September 1968, see page 4, lines 9-20	

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
7th January 1988	19 FEB 1988

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 8702490
SA   19091

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 05/02/88
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 4316964	23-02-82	None		
US-A- 4358486	09-11-82	None		
FR-A- 2230603	20-12-74	DE-A,C	2424602	12-12-74
		US-A-	3873344	25-03-75
		GB-A-	1463840	09-02-77
		CA-A-	1027814	14-03-78
		JP-A-	50041908	16-04-75
DE-C- 666698		None		
CH-A- 456429		None		
BE-A- 840132	16-07-76	LU-A-	77017	22-07-77
		NL-A-	7703177	28-09-77
		FR-A-	2345408	21-10-77
LU-A- 56944	23-03-70	FR-A-	1603820	07-06-71
		GB-A-	1240274	21-07-71
		US-A-	3671302	20-06-72
		DE-A-	1796259	13-04-72
		BE-A-	722879	01-04-69

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82